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Homogeneous oxidation of aromatic hydrocarbons using heteropolyvanadomolybdate-H_2O_2 catalytic system

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Oxidation of alkylbenzenes in the liquid phase in the presence of heteropolyvanadomolybdate-hydrogen peroxide system leads to both side chain and ring hydroxylation. Selectivity pattern exhibited by this system resembles that of the vanadiumperoxo complexes, and differs from that of vanadium silicalite catalysed reactions indicating that the environment in which the active centre is present also plays a major role in the selectivity of the product pattern.

Oxidation is the widely used process in the conversion of aromatic hydrocarbons to industrial chemicals like phenol, terephthalic acid and acetone[1]. Transition metal catalysed reactions of oxygen donors with aromatics afford high selectivities of products derived from side chain oxidation and nuclear hydroxylation of aromatics. The oxidation of phenol to dihydroxybenzenes (catechol and hydroquinone) is of major interest and there are three major hydrogen peroxide processes currently in use[2]. Transition metal substituted silicalites like TS-1 and VS-2 have been used as catalysts for this particular conversion[3,4] and vanadium substituted heteropolymolybdate and tungstate have been used for the hydroxylation of phenol[2].

Heteropoly compounds are also used as catalysts for the oxidation of alkylaromatics[5,6]. Homogeneous oxidation of alkylaromatics using heteropolyvanadomolybdates as catalysts in the presence of hydrogen peroxide has been discussed in this paper.

Materials and Methods

Samples of $H_{3+n}PV_nMo_{12-n}O_{40}$ (n=1-3) were prepared according to the procedure reported in literature[7] and characterised by IR, NMR and UV spectroscopy. UV spectra are given in Figure 1. Oxidation of the substrates was carried out at 303K. The catalyst (0.103 mmol) was dissolved in 5 mL of acetonitrile in a double necked round bottomed flask. To this the substrate (9.1 mmol) was added followed by the addition of hydrogen peroxide dropwise with continuous stirring. After 3 hr, the products were extracted into dichloromethane, washed with water to remove all the catalyst and analysed by GC (Nucon.5700, 2m OV-17, FID). The products were confirmed both by comparison of retention times of the authentic samples and also by GC-MS.

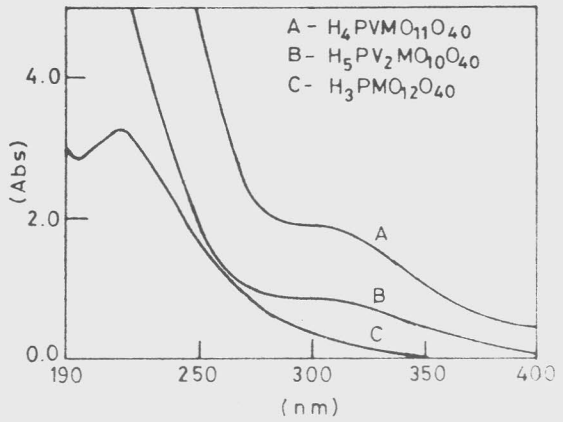


Figure 1—Absorption spectrum of simple and vanadium substituted heteropolymolybdate.

Results and Discussion

In order to assess the hydrogen peroxide efficiency, 27 mmol of hydrogen peroxide was added to 0.103 mmol of the catalyst in water at the required temperatures (315-335K). Decomposition was rapid for $H_6PV_3Mo_9O_{40}$ and the following

trend $H_6PV_3Mo_9O_{40}$ >$H_5PV_2Mo_{10}O_{40}$ >$H_4PVMo_{11}I_{40}$ was observed for the decomposition of hydrogen peroxide. About 30-50% of hydrogen peroxide underwent decomposition under the experimental conditions employed for the oxidation reaction and hence a ratio of 1:3 for the substrate to hydrogen peroxide was employed for the oxidation reaction of aromatic hydrocarbons.

Aromatic hydrocarbons that were used as substrates for this particular type of oxidation were toluene, ethylbenzene, isopropylbenzene, *o,p*-xylenes, chlorobenzene, and condensed aromatics like naphthalene and biphenyl under single phase homogeneous condition. Both side chain oxidation to give ketones or aldehydes, alcohols and ring oxidation (hydroxylation) to give substituted phenols were observed. For example, toluene undergoes both types of oxidation to give benzaldehyde, benzyl alcohol and *o*- and *p*-cresols.

One of the striking features of vanadium substituted heteropolymolybdate-catalysed oxidation of aromatic hydrocarbons is the ability to transfer oxygen to the substrate at room temperature. Both acetic acid and acetonitrile were tried as solvents. Around 43% substrate conversion was observed within two hours in the presence of $H_5PV_2Mo_{10}O_{40}$ as catalyst in acetic acid solvent. Besides aldehyde, *o,p*-cresols, esterification of benzyl alcohol to benzyl acetate was also observed.

All the other reactions were carried out in acetonitrile as solvent, so that it will be convenient to compare the activity of metal centre at different environments, for example, vanadium in heteropolyvanadomoblybdate, vanadium silicalite and vanadium peroxocomplexes[8,9]. Heteropolymolybdates and tungsten substituted heteropolymolybdate showed less than 1% conversion indicating vanadium to be the active centre for this type of oxidation reaction. The effect of vanadium content on the conversion of toluene was studied using $H_{3+n}PV_nMo_{12-n}O_{40}$ (n=1-3) in CH_3CN medium. The results obtained in this study are given in Table I. It is seen for this reaction that an increase in vanadium content seems to increase the percentage conversion. The effect of temperature on toluene conversion was studied by taking $H_5PV_2Mo_{10}O_{40}$ as the catalyst for a period of 1 hr. An increase in temperature increased the conversion but there was

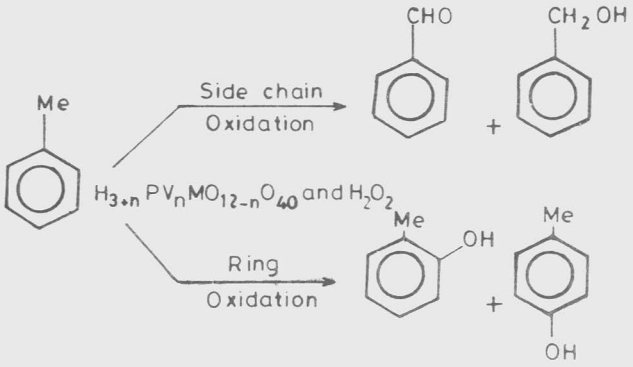


Table I—Effect of vanadium content on the conversion of toluene at 303K for 3hr

Catalyst	Conv. (%)	Product selectivity (%)		
		Benzal-dehyde	*o/p*-Cresols	Benzoic acid
$H_4PVMo_{11}O_{40}$	21.4	10.1	89.2	<1
$H_5PV_2Mo_{10}O_{40}$	25.6	7.7	91.5	<1
$H_6PV_3Mo_9O_{40}$	48.4	8.4	91.6	–

Table II—Effect of temperature on toluene conversion on $H_5PV_2Mo_{10}O_{40}$ catalyst for a period of 60 min.

Temp. (K)	Conv. (%)	Product selectivity (%)		
		Benzal-dehyde	Benzoic acid	*o,p*-Cresols
303	9.8	7.2	0.8	91.0
321	28.4	1.6	7.4	91.0
331	35.4	<1	8.4	91.4

no variation in the selectivity of cresols. Results obtained are given in Table II. Vanadium substituted heteropolymolybdates are found to be effective for the decomposition of hydrogen peroxide[10] and the conversion of substrate after 3 hr remained almost constant in all the cases.

The results obtained on the catalytic behaviour of the three vanadium substituted heteropolymolybdates in the oxidation of ethylbenzene, *o,p*-xylenes, isopropylbenzene and chlorobenzene are given in Table III. Except for chlorobenzene, 40-75% selectivity towards side chain oxidised products was observed for all other substrates. Acetophenone (major product) and 1-phenylethanol were obtained as the side chain oxidised products. In the oxidation of ethylbenzene 2- and 4-ethylphenols were obtained as the hydroxylated products. Both *o,p*-xylenes were oxidised by these compounds to give substituted alcohols and aldehydes; 3,4 and 2,5-dimethyl-

Table III—Catalytic oxidation of alkylbenzenes using $H_{3+n}PV_nMo_{12-n}O_{40}$ at 303K for 3 hr

Catalyst	Substrate	Conv. (%)	Product selectivity (%)		
			Side chain oxidation	Ring hydroxylation	Others*
$H_4PVMo_{11}O_{40}$	Ethylbenzene	17.4	83.0	16.6	<1
	o-Xylene	9.5	67.4	18.1	14.5
	p-Xylene	20.2	75.3	15.2	9.5
	Isopropylbenzene	25.3	43.2	37.3	19.5
	Chlorobenzene	30.7	–	100	–
$H_5PV_2Mo_{10}O_{40}$	Ethylbenzene	25.8	85.9	11.7	2.4
	o-Xylene	12.4	67.4	19.9	12.7
	p-Xylene	23.2	75.3	9.9	14.8
	Isopropylbenzene	26.2	47.9	39.7	12.4
	Chlorobenzene	27.3	–	100	–
$H_6PV_3Mo_9O_{40}$	Ethylbenzene	30.7	88.1	8.6	3.3
	o-Xylene	15.4	69.2	18.8	12.0
	p-Xylene	24.5	71.3	12.3	16.4
	Isopropylbenzene	26.7	48.6	38.8	12.6
	Chlorobenzene	29.4	–	100	–

*Higher oxygenated and unidentified products.

phenols were obtained as the hydroxylated products. Chlorobenzene gave chlorophenols, with the highest selectivity (60%) towards *o*-chlorophenol.

GC-Mass spectra of the products were compared with the mass spectral data reported in the literature for authentic samples. Isomers were fixed both by comparing the retention times of the products with those of authentic samples in GC and also by comparing their mass spectral data reported in literature.

Oxidation of naphthalene and biphenyl led to the formation of 1,4-naphthoquinone as the major product. The results of the conversion for all the three catalysts are given in Table IV. Naphthol could not be detected in this case. Small amounts of phthalic anhydride was observed. A dark tar like material which could not be identified was obtained in this case. An attempt was made to identify this by trying the oxidation of 1-naphthol as the substrate which also resulted in dark tar like material. This may be a reason why naphthol, if at all it was formed during the reaction could not be detected. In the case of V NCL-1[4], phthalic anhydride was observed as the major product along with naphthoquinone. Biphenyl gave 2-phenylphenol and 2,2-biphenylquinone.

The catalytic behaviour of the vanadium centre in the case of heteropolymolybdates was compared with that of the vanadium silicate molecular sieve[8] and that of vanadium in $VO(O_2)_2$ pic.$2H_2O$ complex[9] by taking oxidation of toluene as the example. The results observed for all the three cases are given in Table V. It should be remarked that the mole ratios of substrate to hydrogen peroxide used are different for these different catalysts and, hence, the results obtained are not directly comparable.

In the case of V NCL-1 the side chain oxidation product was the predominant one whereas the behaviour of vanadium in heteropolymolybdate resembled that of the vanadium peroxo complex. This proves that environment of the active metal centre also plays an important role in the selectivity pattern.

The reaction mechanism involving the formation of vanadium hydroxo hydroperoxide and then a vanadium diradical has been proposed by Mimoun *et al.*[9] for the oxidation of alkyl benzene.

Table IV—Oxidation of naphthalene and biphenyl using heteropoly compound as catalyst at 303K for 3 hr

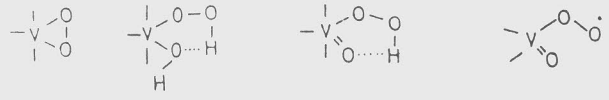
Catalyst	Naphthalene				Biphenyl		
	Conv.	Selectivity (%)			Conv.	Selectivity (%)	
	(%)	NQ	Anhyd.	Others	(%)	Phenol	Quinone
$H_4PVMo_{11}O_{40}$	20:1	48.2	26.4	25.4	14.7	39.9	60.1
$H_5PV_2Mo_{10}O_{40}$	20.9	46.9	27.9	25.2	16.8	35.5	60.5
$H_6PV_3Mo_9O_{40}$	22.1	49.1	29.9	21.0	16.6	38.7	61.3

NQ: 1,4-Naphthoquinone; Anhyd: Phthalic anhydride; Phenol: 2-Phenylphenol; Quinone: 2,2′-Biphenylquinone.

Table V—Comparison of data for the oxidation of toluene with H_2O_2 by various catalysts in CH_3CN

Catalyst/reaction	Conv.	Selectivity (%)			
	(%)	*o,p*-Cresols	Benzyl alcohol	Benzaldehyde	Ref.
VS-2, 333K, 8 hrs	11.7	37	8	52	8
Vanado peroxo complex 303K, 45 min	52	96.2	–	3.8	9
$H_5PV_2Mo_{10}O_{40}$, 3 hrs, 303K	9.8	91	–	7.2	this work

H_2O_2 interacts with the vanadium centre to give vanadium peroxo species which can be given as below.



Peroxo (a) Hydroxohydro-peroxide (b) Oxo hydroperoxide (c) Diradical (d)

The intramolecular hydrogen bonded forms of the type '**c**' are quite likely to be the peroxo species. Oxygen transfer from this vanadium peroxo species to hydrocarbon seems to occur in a bimolecular fashion and the hydroxylation of aromatic hydrocarbons would take place by the homolytic addition of the electrophilic radical species to the aromatic ring.

The vanadium peroxocomplexes which homolytically cleave to give electrophilic reactive species behave differently from the known complexes of molybdenum which are effective for epoxidation of olefins but not as hydroxylating agents. This may be the reason for the ineffectiveness of the $H_3PMo_{12}O_{40}/H_2O_2$ system for these reactions[11,12]. Similar mechanism was suggested by Mimoun *et al.*[9]. Selectivity pattern observed for the heteropolyvanadomolybdate-H_2O_2 system resembles that of the vanadium peroxocomplex, indicating similar behaviour of vanadium under homogeneous condition.

Conclusion

1. Unsubstituted heteropolymolybdate and heteropolytungstomolybdate are not effective for the oxidation of aromatic hydrocarbons whereas vanadium substituted heteropolymolybdates are effective as catalyst. Both side chain and ring hydroxylated products are observed.

2. The catalytic behaviour of the vanadomolybdates are similar to that of vanadium peroxocomplex like $VO(O_2).Pic.2H_2O$ under homogeneous conditions and it differs from that of vanadium substituted silicates. This indicates that besides the active metal centre, the environment in which it is present also affects the selectivity pattern for this type of reaction.

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